

# **Phase Equilibria Diagrams**

**Phase Diagrams for Ceramists**

## **Volume XI Oxides**

**BEST AVAILABLE COPY**

**General Editor**

**Robert S. Roth**

**Associate Editors**

**Howard F. McMurdie, ACerS**

**Helen M. Ondik, ACerS**

**Managing Editor**

**Mary A. Clevinger, NIST**

**Typesetting Editor**

**Kimberly M. Hill, ACerS**

**Graphics Editor**

**Thomas Green, ACerS**

**Editorial Assistant**

**Christina L. Cedeno, ACerS**

**Graphics Associates**

**Evans Hayward, ACerS**

**Nils Swanson, ACerS**

**Text and Typesetting Systems**

**Carla G. Messina, ACerS**

**Graphics Systems**

**Peter K. Schenck, NIST**

**Compiled in the Ceramics Division,  
National Institute of Standards and Technology  
Gaithersburg, Maryland 20899**

**The American Ceramic Society  
735 Ceramic Place, Westerville, Ohio 43081**



## NSRDS

The National Standard Reference Data System comprises a set of data centers and other data evaluation projects coordinated by the Standard Reference Data Program of the National Institute of Standards and Technology (NIST). The aim of this program is to provide reliable reference data on physical, chemical, and materials properties to the scientific and technical communities of the United States. Evaluated data produced under the program are made available in a variety of publications and computer-readable databases through joint projects of NIST and other interested groups, in this case the American Ceramic Society.

The phase diagrams published in this volume were collected and reviewed by the Phase Diagrams for Ceramists Data Center, located in the Materials Science and Engineering Laboratory of the National Institute of Standards and Technology. Significant support from the American Ceramic Society was crucial in providing this important reference information to the ceramics community.

John R. Kumble, Jr.  
Acting Chief, Standard Reference Data Program  
National Institute of Standards and Technology

ISBN 0-944904-90-4

Copyright © 1995, The American Ceramic Society  
All rights reserved.

No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the publisher.

Printed in the United States of America

**BEST AVAILABLE COPY**

BEST AVAILABLE COPY

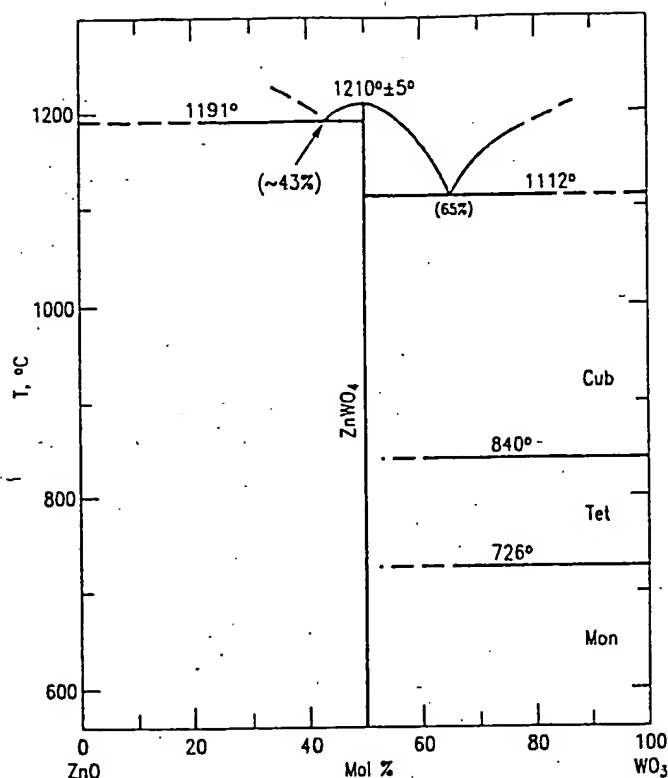
ZnO-WO<sub>3</sub>

Fig. 9261—System ZnO-WO<sub>3</sub>. Mon - monoclinic; Tet - tetragonal; Cub - cubic.

A. V. Shchenev, Yu. F. Kargin, and V. M. Skorikov, *Zh. Neorg. Khim.*, **33** [8] 2165-2167 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)*, **33** [8] 1237-1238 (1988).

The ZnO-WO<sub>3</sub> system was studied by X-ray diffraction, differential thermal analysis, and chemical phase analysis in the concentration range 10-85 mol% WO<sub>3</sub>. The starting materials were highly-pure (for optical glass preparation) grade tungsten(VI) oxide and highly-pure grade zinc oxide. Approximately 12 specimens were prepared at 5-10 mol% intervals. Weighed specimens of the oxides were mixed, ground, and subjected to heating in stages with regrinding at each stage. (No mention was made about contamination.) The temperature was increased from 600°C to (0.9-0.95)*T*<sub>fusion</sub>; the total heating time was about 120 h, and in some cases up to 200 h. X-ray diffraction confirmed that the reaction was complete. The thermal analysis was carried out on a DTA apparatus—at heating and cooling rates of about 7°C min<sup>-1</sup> using platinum crucibles and previously-heated alumina as standard. The X-ray diffraction was carried out on a diffractometer (CuKα radiation, Ni-filter). Tungsten(VI) oxide in the specimens was determined gravimetrically, and zinc oxide by complexometric titration. The only compound formed in this system was normal zinc tungstate ZnWO<sub>4</sub>, with melting point 1210 ± 5°C. Zinc tungstate formed eutectics with the original components: on the tungsten(VI) oxide side at 65 mol% WO<sub>3</sub> and 35 mol% ZnO with melting point 1122°C. The eutectic on the zinc oxide side with composition ~43 mol% WO<sub>3</sub> and 57 mol% ZnO corresponded to a eutectic line which could be followed in the range 52-85 mol% ZnO. The more accurate determination of the composition of this eutectic and the position of the liquidus line was made difficult by the

sublimation of the components at high temperatures. See Figs. 6433 and 9260 for earlier work.

S.K.S.

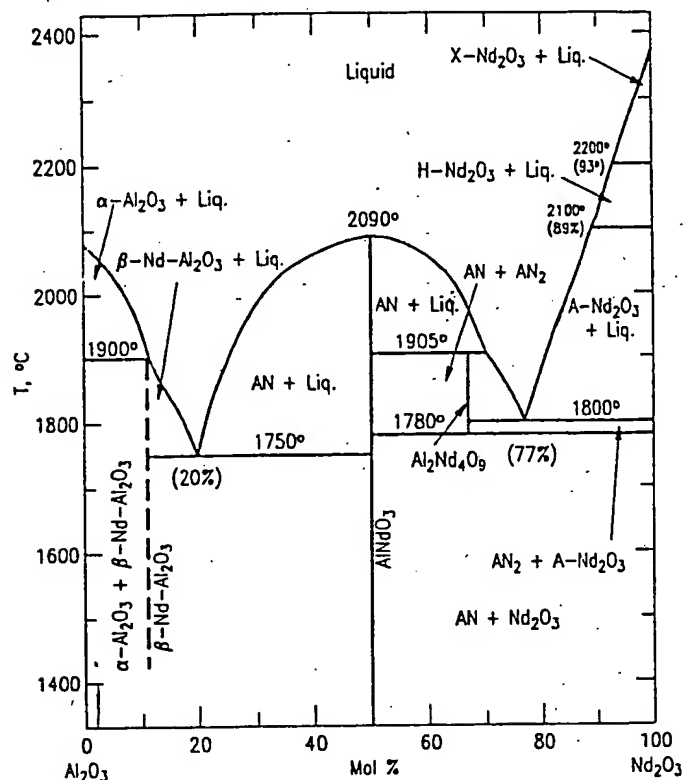
Al<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub>

Fig. 9262—System Al<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub>. AN - AlNdO<sub>3</sub>; AN<sub>2</sub> - Al<sub>2</sub>Nd<sub>4</sub>O<sub>9</sub>; A, H, and X - rare-earth oxide polymorphic forms; A and H are hexagonal; X is cubic; α-Al<sub>2</sub>O<sub>3</sub> - corundum type; β-Nd-Al<sub>2</sub>O<sub>3</sub> - NdAl<sub>11</sub>O<sub>18</sub>.

J. P. Coutures, *J. Am. Ceram. Soc.*, **68** [3] 105-107 (1985).

The tentative phase diagram for the system Al<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub> is presented. The author pointed out the discrepancies in the previous studies.<sup>1-4</sup> The purities of Nd<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> used were 99.9% and 99.99%, respectively. Prior to use, Nd<sub>2</sub>O<sub>3</sub> was annealed at 1200°C for 5 h in order to remove anionic impurities. The samples were prepared in air by co-melting ~30 mixtures of the starting oxides in a laboratory-scale solar furnace. Phase identification was done by room-temperature XRD (Ni-filtered CuKα radiation; goniometer scanning speed 1°C/min in 2θ). The liquidus and solidus lines were drawn from the results obtained by a thermal analyzer associated with a 2 kW horizontal-axis solar furnace. The temperatures were measured with an optical pyrometer under good blackbody conditions (λ pyrometer, 0.65 μm; practical emissivity, 0.99; calibration points, Al<sub>2</sub>O<sub>3</sub> melting point 2053°C and Y<sub>2</sub>O<sub>3</sub> melting point 2440°C). The temperature measurements expressed in the 68 IPTS are at ±10°C. The thermal analyses were performed for each composition under a 2 L/min flow of argon (~100 ppm O<sub>2</sub>) or oxygen (99.9%). The system was scanned over the 0 to 100 mol% Al<sub>2</sub>O<sub>3</sub> composition range in 5 mol% steps except between 10 and 35 mol% Al<sub>2</sub>O<sub>3</sub> and between 70 and 100

**Al<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub> (concl.)**

mol% Al<sub>2</sub>O<sub>3</sub> where 2.5 mol% steps were used. Three compounds, a  $\beta$ -Al<sub>2</sub>O<sub>3</sub>-type compound, the perovskite NdAlO<sub>3</sub>, and Nd<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>, were identified. The exact composition (or composition range) of the  $\beta$ -Nd-Al<sub>2</sub>O<sub>3</sub> phase is not discussed. The perovskite melts congruently at 2090°C; and the other compounds exhibit incongruent melting behavior:  $\beta$ -Nd-Al<sub>2</sub>O<sub>3</sub> at 1900°C and Nd<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> at 1905°C. Nd<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> decomposed below 1780°C into NdAlO<sub>3</sub> and A-Nd<sub>2</sub>O<sub>3</sub>. On the Nd<sub>2</sub>O<sub>3</sub>-rich side, and due to high temperature transitions (A-H at ~2100°C and H-X at ~2200°C) two metatectics are observed on the liquidus line at ~2100°C, 11 mol%, and at ~2200°C, 7 mol% Al<sub>2</sub>O<sub>3</sub>. The author observed for a given composition a depression of liquidus and solidus temperatures due to oxygen dissolution in the melt.

1. N. A. Toropov and T. P. Kiseleva, *Zh. Neorg. Khim.*, **6** [10] 2353-2358 (1961); *Russ. J. Inorg. Chem. (Engl. Transl.)*, **6** [10] 1193-1196 (1961).
2. M. Mizuno, T. Yamada, and T. Noguchi, *Yogyo Kyokashu*, **85** [2] 90-95 (1977).
3. E. Antic-Fidancev and P. Caro, *C. R. Seances Acad. Sci., Ser. C*, **284** [13] 471-474 (1977).
4. J. P. Coutures, E. Antic, and P. Caro, *Mater. Res. Bull.*, **11** [6] 699-706 (1976).

S.K.S.

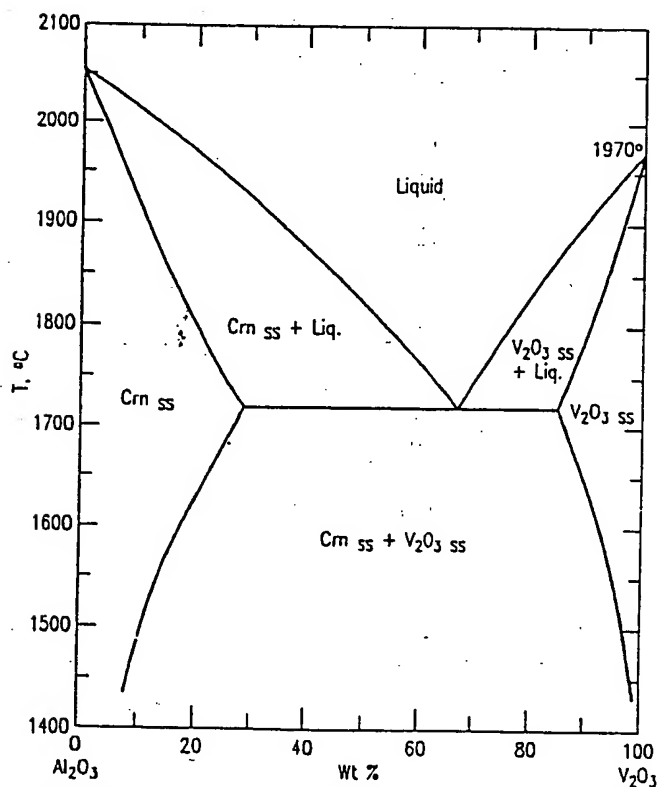
**Al<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub>**

Fig. 9263—System Al<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub>. Crn - corundum (Al<sub>2</sub>O<sub>3</sub>).

A. Muan and M. S. Najjar; "Compositions Involving V<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO", US Patent 5,070,065, 1991.

There are strong crystallographic similarities between V<sub>2</sub>O<sub>3</sub> and other better known sesquioxides, such as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>. They all have the close-packed hexagonal corundum-type structure in which cations are in octahedral coordination. Among the trivalent cations forming these sesquioxides, Al<sup>3+</sup> stands out as being considerably different from the others (Fe<sup>3+</sup>, Cr<sup>3+</sup>, and V<sup>3+</sup>). First, Al<sup>3+</sup> is a noble gas-type ion. Second, it is significantly smaller than the other ions and, hence, can occur fairly readily in four-fold (tetrahedral), as well as six-fold (octahedral), coordination.

There is a lack of complete solid solubility between Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>3</sub>. Corundum solid solution and V<sub>2</sub>O<sub>3</sub> solid solution coexist with a liquid phase along the liquidus surface of the system.

See Figs. 9221 and 9259 for a discussion of experimental methods.

M.S.N.

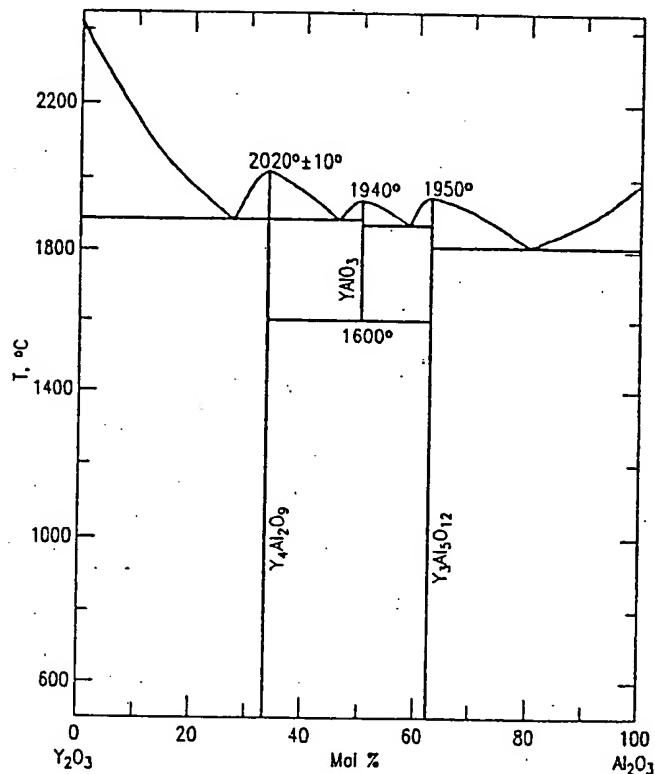
**Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>**

Fig. 9264—System Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>.

I. A. Bondar, L. N. Koroleva, and E. T. Bezruk, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **20** [2] 257-261 (1984); *Inorg. Mater. (Engl. Transl.)*, **20** [2] 214-218 (1984).

The starting materials were Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. Approximately 20 compositions were obtained by solid-phase synthesis by precipitation from nitrates and from the melt. Microscopy, X-ray diffraction, and X-ray spectral analysis were used to analyze products.

See Figs. 311, 312, 2344, and 4370 for earlier studies.

G.L.G.